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New H-Bonded Complexes and Their Supramolecular Liquid-Crystalline Organizations

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Different approaches to the design of liquid crystals by using H-bonds were analyzed. A selection of stilbazoles and pyridine compounds, with one or two chelating positions, were used as H-acceptors in mixtures with carboxylic acids. The noncovalent complexes in question afforded calamitic mesomorphism (N, SmA and SmC) as well as a lamellar mesophase (SmCP). Additionally, the liquid crystalline behaviour of the new 2-hydroxy- and 2-aminopyridine compounds as pure materials is also discussed. Useful results concerning the design and stability of noncovalent calamitic and bent-core liquid crystals are reported. To induce the bent-core liquid crystalline order, the conformational flexibility around the H-bond must be controlled. The new liquid crystals were characterized by IR spectroscopy, optical microscopy, calorimetry, X-ray diffraction and dielectric spectroscopy.

Introduction

Supramolecular chemistry has found in hydrogen bonds an extraordinary tool to generate many original and attractive architectures and functionalities. Furthermore, the use of appropriate H-donor and H-acceptor structures enables numerous calamitic and columnar liquid-crystalline mesophases to be stabilized[1] (Figure 1). These soft materials have broadened the possibilities for structural design and macroscopic arrangement through this noncovalent interaction. One particularly attractive possibility is the use of nonmesomorphic single components to form such liquid-crystalline systems.

In recent years, a new type of mesogenic material has emerged in this field, the so-called banana-shaped liquid crystal.[2] This name comes from the bent-shape of the molecules involved in generating these new phases. Through a compact arrangement that restricts their rotational freedom, these molecules offer new types of mesophases and phenomena that are attracting the interest of chemists and physicists. A large variety of columnar and lamellar molecular packing arrangements, some of which exhibit supramolecular chirality, have been reported since the pioneering results of Niori et al.[3]

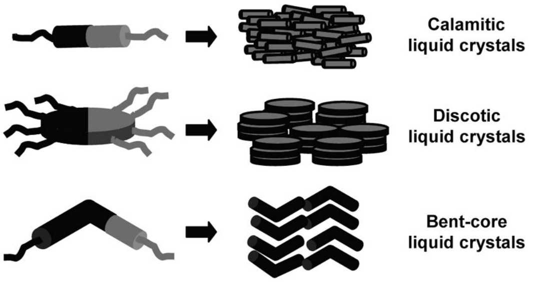

Figure 1. Different liquid crystals generated by using H-bonds.

Current research in this new field is focused on numerous areas. Some examples concern the characterization and understanding of the new types of liquid crystalline phases, their physical properties, the exploration of their practical applications and, of particular interest to chemists, how to control all of these properties through suitable molecular design.

In this respect, hydrogen bonding has proved to be a useful tool to tailor properties. The use of carboxylic acids and stilbazoles **I** and **II** (Figure 2), which act as H-donor and H-acceptor, respectively, has afforded bent-shaped complexes that arrange in these new mesophases, even with side-chain bent-shaped liquid-crystal polymers.[4,5] The SmCP phases are the most common and widely studied of this new type of mesophase. This phase is characterized by its tilted lamellar and polar packing. Depending on the direction of polarization in adjacent layers, the mesophase can have either a ferro- and/or antiferroelectric ground state. On the other hand, depending on the tilt sense of the molecules in adjacent layers, this supramolecular arrange-

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ment could be racemic (SmC_AP_F or SmC_SP_A phases) or homochiral (SmC_SP_F or SmC_AP_A phases).[2] This combination of tilt and molecular tip direction in the smectic layers causes extraordinary properties in the SmCP phase, for example, to exhibit electrooptic switching under an applied external field.

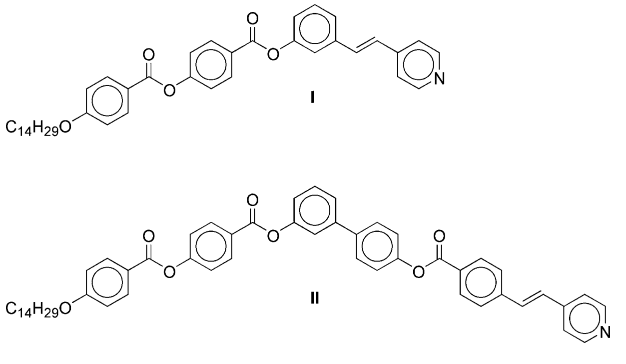

Figure 2. Chemical structures of the H-acceptors used in a previous study.

In this respect, the validity of the new banana-shaped liquid-crystal materials prepared by the H-bonding approach was also emphasized, proving that these materials show an electrooptic and antiferroelectric response similar to those described for covalent bent compounds in a SmC_AP_A phase.[5] Interestingly, our previous studies have allowed us to highlight the versatility of the H-bonding approach to study new bent-core liquid crystals.

In a further step, the search for new H-acceptors that they will allow the properties to be modulated was planned. With this target in mind, different approaches have been proposed in an effort to build the bent-structure of the complex. The possibility of creating bent-shaped liquid crystalline materials by the formation of two H-bonds with bis(pyridine) acceptors or, alternatively, by linking a carboxylic acid to H-acceptors through single or double chelation, have been envisaged.

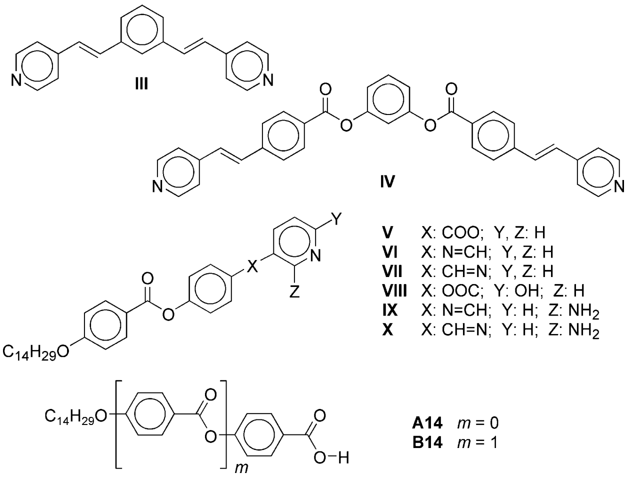

Figure 3. Chemical structures of the H-acceptors and H-donors used in this work.

In order to assess the first possibility, stilbazoles **III** and **IV** were prepared by taking into account our previous results (Figure 3). Likewise, given that complexes containing five aromatic rings were sufficiently large to induce bent-core liquid-crystalline arrangements,[4,5] benzoic acids **A14** and **B14** were chosen as H-donors. For the second approach, compounds **V**, **VI**, **VII, VIII**, **IX** and **X** were designed and prepared for mixing with acid **B14**.

Results and Discussion

The new H-bonded materials reported here are identified by using a notation corresponding to both the H-acceptor and the H-donor, as they are labelled in Figure 3.

All of the complexes prepared were first studied by optical microscopy. The solid samples should melt cleanly without the appearance of biphasic regions, which would otherwise have indicated the presence of nonstoichiometric complexes. Only those mixtures that resulted in homogeneous materials are included in the discussion.

The formation of hydrogen-bonding interactions in the neat materials was investigated by infrared spectroscopy. IR spectra show features that are characteristic of carboxylic acid–pyridine systems. The complexes show two absorptions around 1950 and 2500 cm^{-1}, which correspond to the N···H–O interaction, whereas carboxylic acid dimers exhibit a band at 2650 cm^{-1} (O–H). Likewise, bands corresponding to the C=O absorption of acid dimers (around

Table 1. Transition temperatures and the associated enthalpy values (in parentheses) as determined by DSC for the H-acceptors, H-donors and the complexes derived from them.

Compound	Phase transition,[a] temperature [°C] and enthalpy [$kJ\,mol^{-1}$][b]
III	C 208 [25.0] I
IV	C 192 [100.6] I
V	C 114 [64.1] SmA 148 [7.0] I
VI	C 87 [40.1] SmA 136 [0.54] N 142 [1.1] I
VII	C 96 [75.4] SmA 146 [5.1] I
VIII	C 148 [25.2] SmC 230 [5.1] I
IX	C 148 [54.6] N 156 [1.2] I
X	C 195 [43.3] SmC-N 203 [1.1][c] I
A14[6]	C 97 SmC 139 I
B14[6]	C 118 SmC 209 N 214 I
III-A14	C 142 [66.3] I
III-B14	C 154 [33.5] SmC 172 N 176 [6.2][c] I
IV-A14	C 174 [72.5] I
IV-B14	C 171 [27.3] SmA 205[d] [8.4] I
	I 204 [4.4] SmA 180 [6.4] SmC 149 [20.1] I
V-B14	C 109 [125.7] SmA 131 [0.25] N 150 [2.] I
VI-B14	C 104 [86.8] SmC 118 [0.76] N 147 [2.6] I
VII-B14	C 92 [72.2] SmC 119 [0.34] N 142 [3.2] I
VIII-B14[e]	C 123 [52.6] SmC 203.7 [16.8] I
IX-B14	C 105 [89.7] SmCP 128 [17.1] N 140 [0.77] I
X-B14[e]	C 120 C + M 150 C + I 180 I

[a] C: crystalline phase, SmCP: smectic C polar mesophase, SmC: smectic C mesophase, SmA: smectic A mesophase, N: nematic mesophase, I: isotropic liquid, M: mesophase. [b] Reported are the onset values for transitions observed for the second-scans at 10 °C min^{-1}. [c] Combined enthalpies. [d] Broad peak. [e] Data corresponding to a homogeneous blend of the components not consistent with the expected H-bonded complex.

1683 cm^{-1}) were not detected for the complexes. Furthermore, variable-temperature IR spectra reveal that dissociation of the self-assembly is not observed either in the solid or the mesophase.

The thermal properties of the new materials were determined by polarizing optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction in the mesophase.

The majority of the complexes synthesized form liquid crystals (see Table 1), exhibit soft phases over temperature ranges that are different to those at which the individual components display calamitic phases (see Table 1). Several representative optical textures observed for these materials are shown in Figure 4.

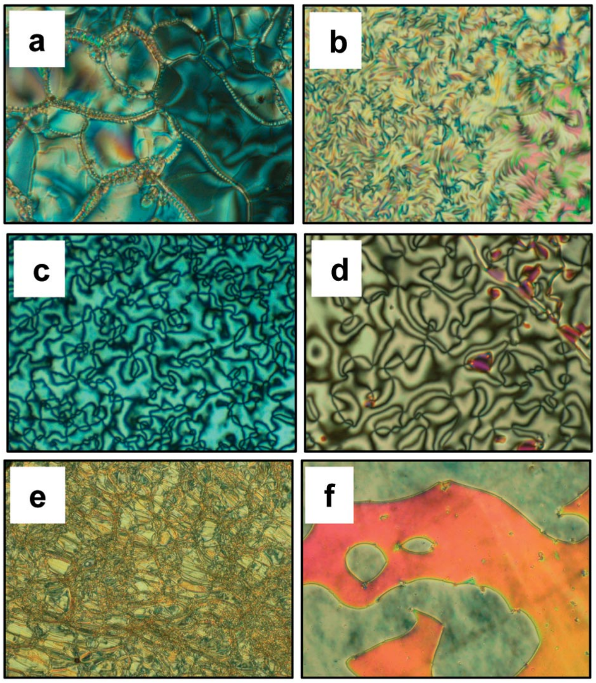

Figure 4. (a) Complex **IV-B14** at 178 °C in the SmC mesophase; (b) complex **VII-B14** at 119 °C, showing the transition from the N to the SmC phase on cooling; (c) complex **VI-B14** at 144 °C in the N mesophase; (d) complex **V-B14** at 145 °C in the N mesophase; (e) complex **IX-B14** at 112 °C in the SmCP phase; (f) complex **IX-B14** at 135 °C in the N phase.

Liquid Crystals Based on Compounds III and IV as the H-Acceptors

As reported in Table 1, only some of the materials prepared by using these H-acceptors (**III-A14**, **III-B14**, **IV-A14** and **IV-B14**) induced liquid-crystalline order and none of the mesophases were identified as any of the typical bent-core liquid-crystalline phases. Double complexation either prevented mesomorphism or led to less-ordered calamitic phases (SmC, SmA or N).

Typical *marbled* and *Schlieren* optical textures with only 4-brush defects were detected for the N mesophase. In the case of the lamellar phases, a high tendency to afford homeotropic alignment was detected for the SmA mesophase, whereas the *Schlieren* textures identified the SmC phase (Figure 4). These assignments were confirmed by X-ray diffraction patterns.

When the transition temperatures of these materials are compared, some aspects can be pointed out. Firstly, both of the bent stilbazols studied allow strong packing within the solid, but only when the long acid **B14** is present are the intermolecular interactions sufficiently strong to give rise to liquid-crystal order before melting. Secondly, for either **III-B14** or **IV-B14** these interactions stabilize the calamitic mesophases by around 20–30°.

The literature on banana-shaped liquid crystals contains many examples of bent molecules that exhibit calamitic mesophases.[2,7,8] Some authors have attributed this fact to open-bent cores leading to linear molecular conformations. This proposal could also be extended to our bis(chelating) systems. Thus, the conformational flexibility around the hydrogen bond could open up the central bend angle to give rise to linear structures rather than bent ones. This situation would prevent the strong packing required for the formation of bent-core mesophases (Figure 5).

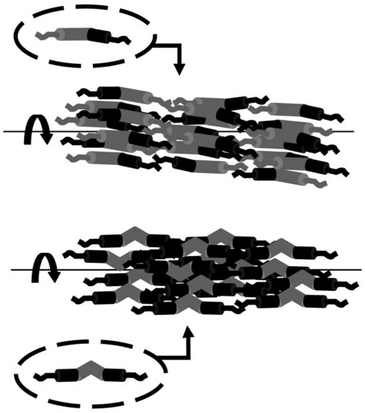

Figure 5. Schematic representation of the molecular packing proposed for the calamitic mesophases induced by H-bonded complexes with molecular conformations close to the linear materials based on **III** and **IV** (top) and based on **V-VII** (bottom). Linear structures allow the rotational freedom that leads to calamitic liquid crystals instead of bent-core liquid-crystal phases.

These results are in good agreement to those recently reported by Bruce et al.[9] By using dipyridyloxadiazole linked to different benzoic acids, only calamitic mesophases occur. H-acceptors **II** and **IV** are more bent and larger than dipyridyloxadiazole; however, this is still not sufficient to induce bent-core mesophases versus calamitic ones. This is also the case when a large number of aromatic rings (up to 9) are present (**IV-B14**).

Liquid Crystals Based on Compounds V, VI and VII as H-Acceptors

By taking into account the above results, the presence of conformationally restricted structures should be more appropriate to achieve bent-core mesomorphism. For this purpose, different linear pyridine derivatives such as **V**, **VI** and **VII** were synthesized. These pyridine H-acceptors would constitute one of the lateral parts of the bent complexes, where the presence of covalent bonds could tighten the central angle.

Sufficiently long structures are needed to induce B-type mesophases,[8] but as H-bonded complexes with five-ring systems are large enough to promote the SmCP mesophase, acid **B14** was used as an H-donor in this case.

Compounds **V**, **VI** and **VII** form liquid-crystal phases in their own right (Table 1). In all cases, the presence of a SmA phase was detected by POM and X-ray studies. A layer spacing of around 38 Å, close to the molecular length estimated from Dreiding models (≈ 36 Å), was determined in the mesophase.

When these pyridine compounds were mixed with acid **B14** (molecular length ≈ 34 Å), three new H-bonded materials were obtained. All exhibit liquid-crystalline behaviour, but as observed from their optical textures they show calamitic phases (Figure 4).

All of these materials show an N phase, but whereas the presence of imine groups promotes an additional tilted smectic C order (**VI-B14** and **VII-B14**), diester **V** induces an orthogonal arrangement (SmA). A layer thickness of around 49.9 Å was determined for the mesophase formed by this complex. Likewise, all of these materials exhibit mesophase ranges and clearing temperatures very similar to those shown by the H-acceptors. On the basis of these data, we propose that within the mesophases of **V-B14**, **VI-B14** and **VII-B14**, both components adopt a linear disposition rather than a bent orientation upon complexation.

These results seem to confirm that conformational flexibility in the bent-core structure does not stabilize the molecular packing responsible for the bent-core mesosphere (Figure 5).

Interestingly, comparison of the thermal properties of the complexes that are similar in length (**III-A14**, **V-B14**, **VI-B14**, **VII-B14**) with those of complex **I-A14** (Figure 6) shows that, as expected, the symmetric complex has the most efficient packing in the solid phase but undergoes a direct transition to a liquid at 142 °C. Likewise, this temperature is very close to the clearing points of the unsymmetrical complexes but they can stabilize calamitic liquid-crystal order prior to the liquid phase. However, unsymmetrical complex **I-A14**, which melts to a SmCP phase at around 90 °C, exhibits the lowest stabilization of mesogenic order. It can therefore be concluded that the extension of the bent structure has an important effect on the stabilization of bent-core liquid-crystalline packing.

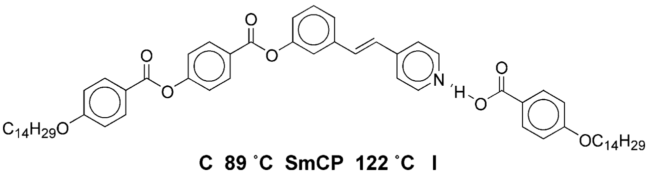

Figure 6. Complex I-A14 and its liquid-crystalline properties.

Liquid Crystals Based on Compounds VIII, IX and X

To decrease the flexibility in the H-bonded environment and to enforce the bent-shape of the complexes, pyridine derivatives **VIII**, **IX** and **X** were prepared. In all cases, bent-core structures should be formed on complexation with acid **B14** by double H-bonding.

The 2-hydroxypyridine derivative and the two 2-aminopyridines form liquid crystalline phases by themselves, with a higher stabilization of the soft order than with compounds **V**, **IV** and **VII** (Table 1).

2-Hydroxypyridine systems have been widely studied in the solid state and in solution,[10] which is in marked contrast to the small amount of interest in the liquid-crystal field.[11] However, a broad SmC phase was attributed to **VIII** on the basis of POM, DSC and X-ray studies. From the latter studies, a layer spacing of 46 Å within the tilted mesophase was determined and this is larger than the molecular length estimated from Dreiding stereomodels (around 38 Å).

IR experiments of compound **VIII** in KBr at different temperatures revealed that the raw materials did not show any absorbance around 1660 cm^{-1} (which is characteristic for 2-pyridone tautomers) but bands at 3100–3000 and 2600–2500 (broad) cm^{-1} were observed (Supporting Information, Figure S2). However, thermal treatment of these samples led to the appearance of an intense band at 1650 cm^{-1}, which shifted to 1686 cm^{-1} upon heating to the isotropic liquid. This new absorption remained when the sample was cooled to room temperature. These spectroscopic data are in good agreement with those reported in the literature for dimers of 2-pyridone structures in the solid phase.[10a,10b,12]

The 2-aminopyridine system was successfully used to promote mesomorphism through noncovalent interactions, especially with melamine derivatives.[1,13] Compounds **IX** and **X**, however, are the first examples of simple structures to link this family of systems. Both materials form an N mesophase in a narrow temperature range − in contrast to compound **VIII**, which allows a broad and strong stabilization of the liquid-crystal order. Likewise, compounds **VIII** and **IX** melt around 150 °C, but compound **X** derived from the diaminopyridine significantly stabilizes the solid packing.

To study structural aspects of these new 2-aminopyridine compounds in the condensed phases, IR studies at variable temperatures in KBr were performed. By taking into account results reported by Abdulla et al. for 2-aminopyridines,[14] the formation of dimers could be considered to result form the absence of absorptions at 3500 cm^{-1} (Figure 7; Supporting Information, Figure S5). Unfortunately, the crystallization of **X** prevented further evidence from being obtained for this dimerization by X-ray diffraction on the SmC mesophase. Additionally, for compound **X**, the 2-pyridone dimer seems to be the only one present (bands at 3200–3140 cm^{-1}; Supporting Information, Figure S5), but associations of different tautomers can be proposed for **IX** owing to the presence of an extra absorption at 3340 cm^{-1} (Figure 7).

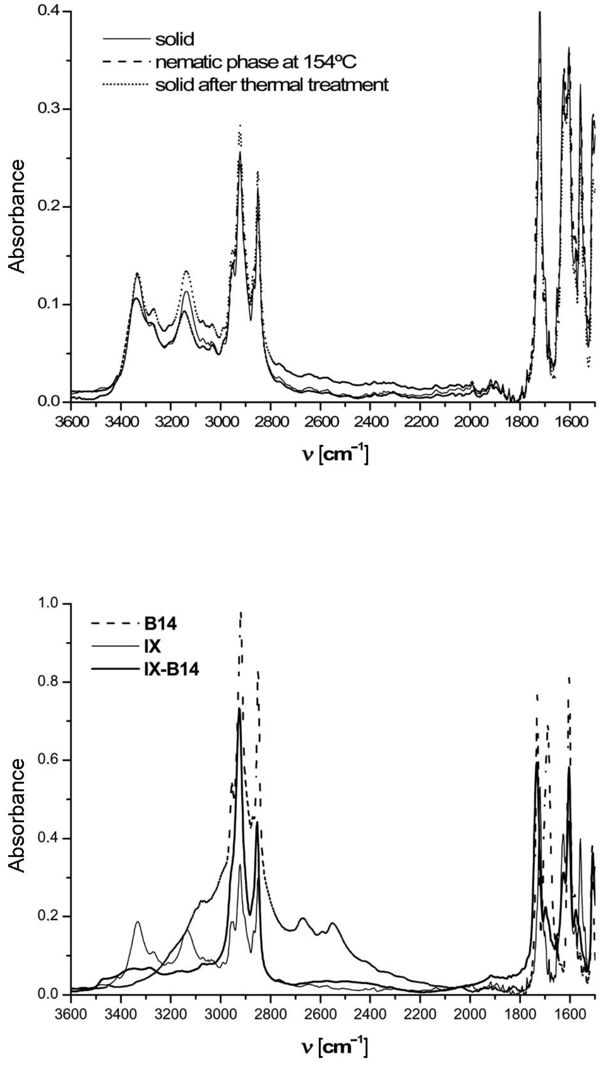

Figure 7. IR spectra (KBr) of compound **IX** at different temperatures (top) and that of complex **IX-B14** and its components (**B14** and **IX**) at room temperature (bottom).

On the basis of these results, the molecular dimerization of compounds **VIII**, **IX** and **X** within the condensed phase can be proposed as the origin of the stabilization of the mesophase order in these materials (Figure 8). When these three 2-substituted compounds were mixed with acid **B14**, three new materials were obtained and they exhibit rather different behaviours. The blend of **X** and **B14** did not give rise to an appropriate material for study. A phase sequence in which crystalline and liquid-crystalline phases coexist was observed by POM on repeated heating and cooling scans (Table 1). IR studies in KBr (Supporting Information, Figure S5) suggest incomplete complexation of the two components. In contrast, **VIII-B14** promotes a calamitic SmC phase and **IX-B14** gives rise to an N phase at high temperature but a B-type mesophase occurs at low temperatures (Figure 4e, f).

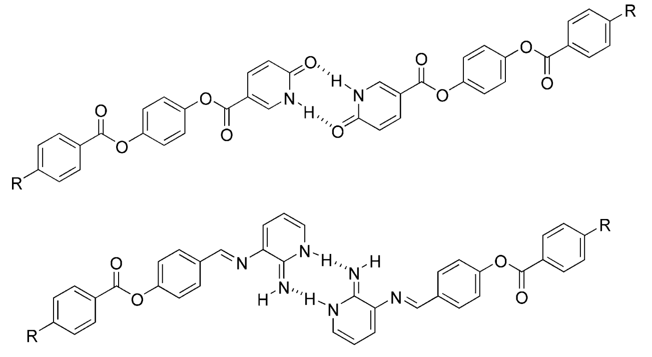

Figure 8. Chemical structure proposed for the dimers formed for compounds VIII and X in the condensed phases.

To gain better insight into the cause of the unexpected calamitic order afforded by **VIII-B14**, this material was studied by X-ray diffraction and IR spectroscopy at variable temperature. The tilted lamellar phase was assigned on the basis of both the optical textures and the X-ray diffraction patterns, which showed a layer thickness of 42 Å – very similar to the data measured for compound **VIII**.

Furthermore, IR studies at variable temperature revealed some other noteworthy aspects. Along with the presence of the 2-pyridone tautomer (bands around 1650 cm^{-1}), an absorption at 1716 cm^{-1} corresponding to the carboxylic acid can be observed (Supporting Information, Figure S3). This peak is far from the one attributed to the dimeric form of acids (around 1689 cm^{-1}).

Similar bands have been reported for 1:1 mixtures of 2-hydroxypyridine and carboxylic acids in the solid phase.[12] Furthermore, X-ray data[15] for this type of material revealed that carboxylic acids are not capable of breaking the strong dimerization in this type of pyridine derivative and the interactions between the two components are limited to weak –N–C=O···HOOC associations. By taking all of these results into account, the calamitic mesophase presented by the material afforded by mixing **VIII** and **B14** is more consistent with the formation of structures similar to that shown in Figure 9 than a bent-core complex.

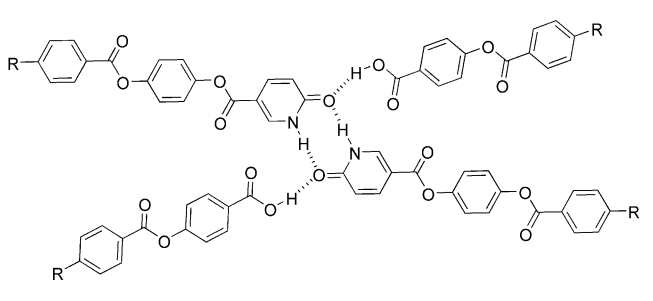

Figure 9. Chemical structure proposed for the material afforded by mixing VIII and B14.

This is not the case for **IX-B14**. IR studies, X-ray diffraction and DSC measurements support the formation of a proper bent-core complex as the origin of a bent-core mesophase. It can be seen in Figure 7 that the peaks at 3400 and

3100 cm^{-1}, which correspond to the amino group of **IX**, as well as those associated to dimers of acid **B14** at 2600–2500 cm^{-1} disappear on mixing, whereas broad absorptions at 2450 and 1900 cm^{-1}, associated with the N···H–O interactions, are also observed.

DSC studies show a large enthalpy change (17 kJ mol^{-1}) on cooling the nematic phase (Figure 10b), which gives rise to a lamellar mesophase for which up to three orders of reflections (*hkl,* 001, 002 and 003) were detected by X-ray studies (Figure 10a).

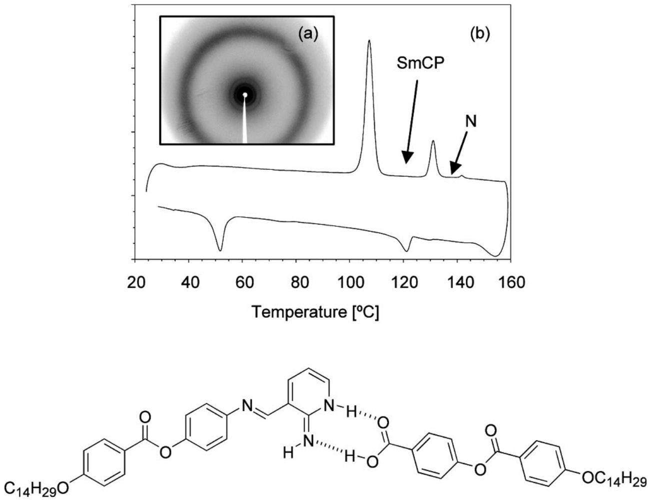

Figure 10. Chemical structure proposed for complex **IX-B14**. X-ray diffraction pattern of a nonoriented sample in the SmCP phase at 110 °C (a) and DSC traces at a scanning rate of 10 °C min^{-1} (b).

The lamellar mesophase is clearly switchable under electric fields. The texture observed under a triangular field (50 Hz, 30 Vpp µm^{-1}) is shown in Figure 11b. Crosses with the extinction brushes tilted with respect to polarizer and analyzer can be observed. However, until this maximum field was applied, a depolarization current could not be observed. Further increases in the field led to the destruction of the sample. It is also important to note that the compound is not very stable under electric fields (the transition temperatures change and many bubbles appear).

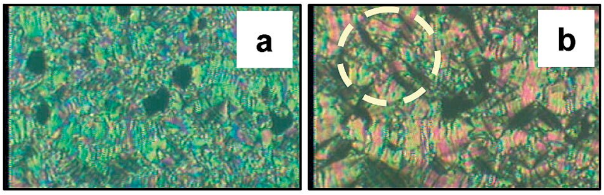

Figure 11. Optical photomicrographs obtained in the liquid-crystal phase of complex **IX-B14** at 111 °C: (a) in the absence of an electric field; (b) upon application of a square wave (30 vpp µm^{-1}, 50 Hz). Extinction brushes are rotated at an angle with respect to polarizer and analyzer (in the circle).

A plot of dielectric permittivity at 1 and 10 kHz versus temperature, on both heating and on cooling, is given in Figure 12. At the N-SmCP phase transition, the low frequency permittivity decreases. This fact is related to a decrease in some spurious contribution associated with the conductivity. At 10 kHz, the permittivity is larger in the SmCP phase than in the N phase, as expected for these bent-core phases because of the polar correlation between molecules. Although we could not measure the spontaneous polarization, there is sufficient information to infer the SmCP structure for this mesophase.

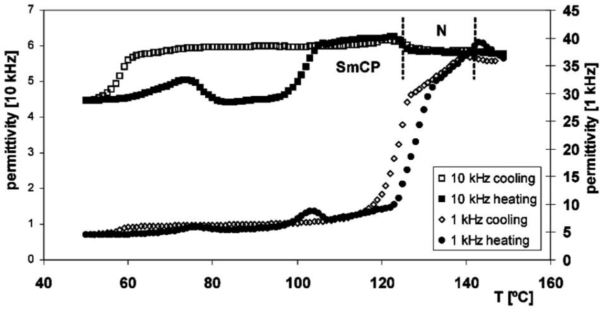

Figure 12. Temperature behaviour of the dielectric permittivity for complex **IX-B14**.

In contrast to other H-bonded bent-core materials based on pyridine–carboxylic acid complexation[5] this complex exhibits a significant instability under subsequent electric field application. This instability should be attributed to the new H-bonded system presents in **IX-B14** where different weak bonds involving H-atoms are present. Interestingly, few data concerning the application of electric fields on 2-aminopyridine–carboxylic acid exist[1] so these results should be considered for future research not only for liquid crystals but for alternative H-bonded supramolecular systems in general.

Conclusions

In this work we showed how noncovalent interactions play a unique role in constructing supramolecular systems with liquid-crystal order. Thus, H-bonds have offered a convenient and versatile approach to the design and understanding of liquid-crystalline behaviour in general, and bent-core mesomorphism, in particular.

Interestingly, the stabilization of calamitic liquid-crystal order is possible by H-bonding dimerization of single and simple 2-hydroxy- and 2-aminopyridine compounds that open new perspectives in the engineering of these soft materials.

On the other hand, this paper demonstrates that even though different approaches to the design of H-bonded bent-shaped liquid crystals exist, the conformational flexibility around this noncovalent interaction must be restricted to induce bent-core liquid-crystalline order. The formation of single H-bonds either in the apex position or within both lateral parts of V-shaped structures do not afford the rigid bent-structures needed to promote B-type mesophases and thus less-ordered calamitic soft phases occur. Additionally, the appropriate selection of the chemical structure around the H-bonded moiety could strongly determine the stability of this kind of material in electric fields.

Experimental Section

The synthetic routes for the H-acceptors are shown in Schemes 1 and 2. In all cases, synthetic methods reported in the literature or adaptations of these methods were followed. The carboxylic acids used in this research were prepared according to synthetic methods from the literature.[5,16,17] Experimental details are reported in the Supporting Information. The thermal properties of all these compounds are gathered in Table 1.

The complexes were prepared by dissolving the precise equimolecular proportions of the corresponding components in freshly distilled THF. The blends were mechanically stirred overnight at room temperature. In the case of compounds **IX** and **X**, the mixtures were stirred at 60 °C for 3 d due to the low solubility of the pyridine components. The solvent was subsequently removed under reduced pressure in all cases. The residual solvent was removed by heating the sample at 40 °C under vacuum overnight.

Supporting Information (see footnote on the first page of this article): Synthetic procedures, thermal, spectroscopic and X-ray data of different materials and techniques used in their characterization.

Acknowledgments

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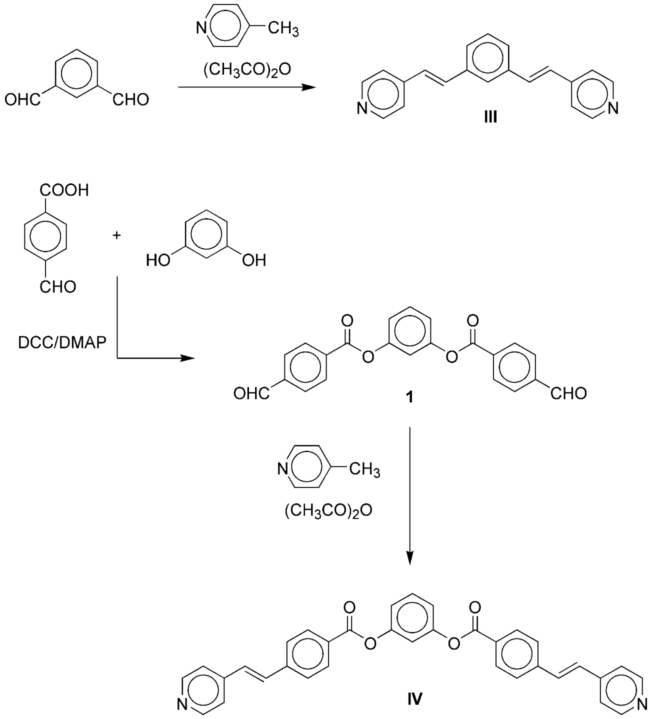
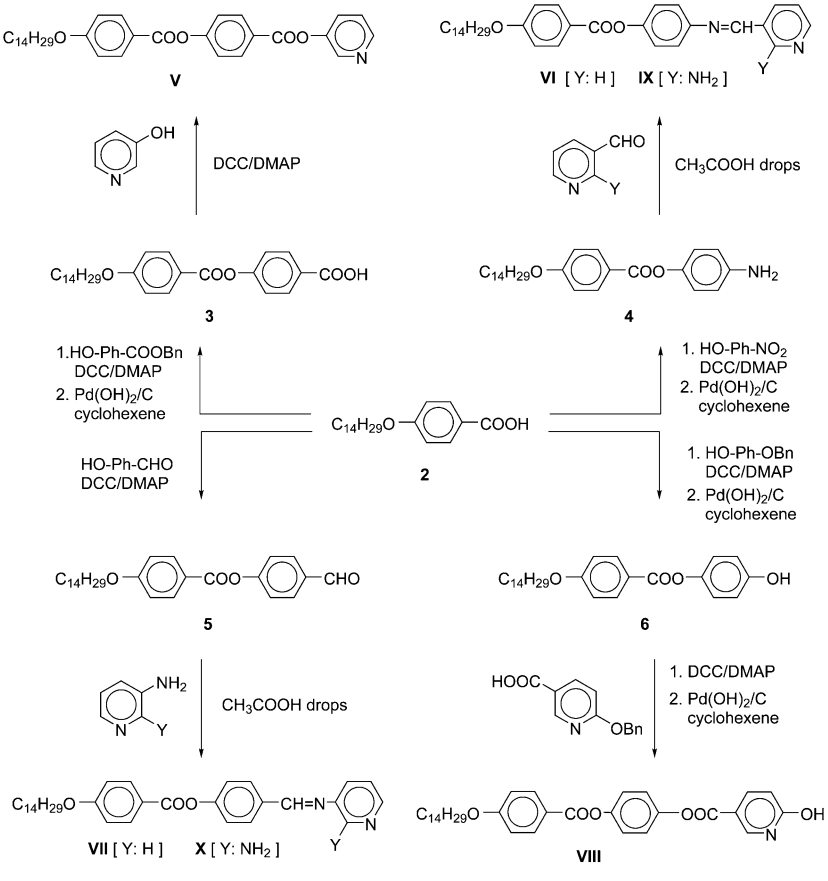


Scheme 1. Routes for synthesis for compounds **III** and **IV**.



Scheme 2. Routes for synthesis for compounds **V**–**X**.

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